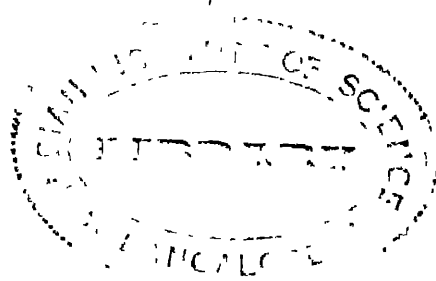


A STUDY
OF THE
OPTICAL PROPERTIES OF
POTASSIUM VAPOUR

BY
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*Thesis approved for the Degree of Doctor of Science in the
University of Madras.*

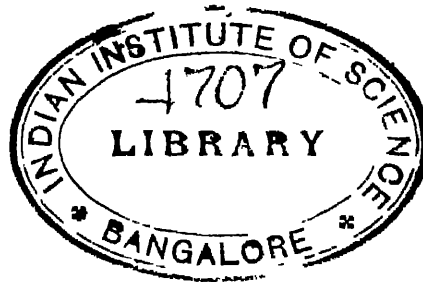


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PREFACE.

THE work contained in this thesis was commenced two years back, and the results achieved in these investigations till December 1922 were embodied in a series of papers submitted to the Philosophical Magazine, and other journals, the first of which, on "Absorption of Potassium Vapour in the Visible and the Ultra-violet Regions" (with reference to principal series), will appear in the May number of the same journal. A few important results realized by me in the course of these experiments were also published in *Nature*, 19th August 1922. Similarly a note which was submitted to the *Astro-physical Journal* of America in August last appeared in the April number. A preliminary statement of these results was made before the Indian Science Congress, held at Lucknow, January 1923. This thesis treats critically and somewhat comprehensively these and other investigations since conducted in this laboratory. The importance of the results accomplished in these investigations is clearly brought out in the thesis, and is also briefly indicated in the summary and conclusions at the end.

In the preparation of this thesis, besides the various journals and periodicals, I have used the following books :—

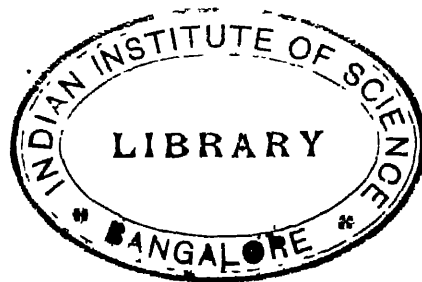
A Study of Spectrum Analysis (W. Marshall Watts) ; *Report on Series in Line Spectra* (A. Fowler) ; *The Theory of Spectra and Atomic Constitution* (Niels Bohr) ; *A Treatise on the Analysis of Spectra* (W. M. Hicks) ; *Handbuch der Spectroscopie* (Vols. V and VI) (H. Kayser). I am under great obligation to two of my Assistants (Messrs. G. Subrahmanyam and

D. Gunnayya), who have given freely and generously of their time and energies, and rendered invaluable assistance in the different stages of the work. My thanks are also due to Dr. C. V. Raman, of the University College of Science, Calcutta, for the encouragement he gave me in the pursuit of this investigation during his visit to Vizianagram in October last; and to Dr. S. R. U. Savor, of the Presidency College, Madras, for kindly placing his library at my disposal in May last.

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26th April 1923.

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A STUDY OF THE OPTICAL PROPERTIES OF POTASSIUM VAPOUR.

INTRODUCTION.

While a study of the physical and chemical properties of matter produced our atomic theory, which postulates the dogma of the indestructible and indivisible atom, it is the study of the spectra of different elements that tells us that the atom could not be the ultimate unit of matter but that it has a very complex structure. When the atom or molecule of an element is excited, the radiation emitted is found to consist of a number of superposed waves of definite frequencies peculiar to the element and to the kind of excitation. The spectra emitted by different elements are indeed, as Professor Hicks says, documents containing implicitly the description of the constitution of the atom written in as yet unknown language and unknown script. The brilliant researches of Franck and Hertz, McLennan and Bergen, Davis and Goucher, on "Ionisation Potentials," and those of Moseley on X-rays, furnish the most convincing evidence that the study of the spectra gives us a clear insight into what is happening in the ultra-microscopic region of matter and very valuable information regarding the sub-atomic structure.

According to Rutherford's conception of the atom, the atom of an element is a solar system on a very miniature scale, the atom consisting of a central positively charged body of extraordinarily minute dimensions, surrounded by a number of negative electrons, or corpuscles as they are called, revolving in closed orbits round the central nucleus. The dimensions of the nucleus are supposed to be very small in comparison with the dimensions of the atom, and almost the whole mass of the atom is supposed to be concentrated in the nucleus, which has a positive charge of such a magnitude that the number of electrons in a neutral atom is equal to the number of the element in the periodic table. This conception of the atom is mainly due to Rutherford's researches on radio-active substances. Suffice it to say for the present that the problem of radiation provides a most convincing evidence of the general correctness of this conception of the nuclear atom. During the last five years, Bohr and Sommerfeld have, with the aid of the Quantum Theory of Radiation, led an enquiry into the possibilities of this nuclear atom, and have developed a Theory of Spectra which leads to formulæ of the type

$$\nu = f_{k^*}(n'') - f_{k^*}(n')$$

(where n' and n'' are whole numbers; the various lines of the series being obtained by allowing the first term $f_{k^*}(n'')$ to remain constant, while a series of consecutive whole numbers are substituted for n' in

the second term); representing the complex spectra of different elements quantitatively. The spectrum emitted by any element can be sorted out into different series of lines by their different electrical, magnetic and other properties, of which four are now recognized as chief series—

Principal	(1,s)—(m,p)
Diffuse	(2,p)—(m,d)
Sharp	(2,p)—(m,s)
Bergmann	(3,d)—(4,f)

and combinations like (3,d)—(m,p), (1,s)—(m,s), (2,p)—(m,p) also are recognized. The terms (m,s), (m,p), (m,d), may have double or multiple values owing to different possible orientations of the vibrating electron with regard to the nucleus.

According to our present ideas regarding the origin of spectral lines, the emission of radiation of frequency (1,s)—(m,p) results when the electron falls from the (m,p) ring to the (1,s) ring. In the unexcited atom of an element, no electron exists outside the (1,s) orbit, which represents the outermost stable and innermost unstable orbit of the normal atom. The series (1,s)—(m,p) is of fundamental importance in view of the fact that a knowledge of the wave-lengths of these lines in the spectrum of an element enables us to calculate the limiting frequency $\nu = (1,s)$ for that element, from which we can find the ionization potential for it, from the well-known quantum relation $h\nu = eV$.

It is therefore of importance to identify the wave-lengths of this series in the spectra of as many of the elements as possible. And for the elements for which the series is known, the lines of the principal series are strongly absorbed by the non-luminous vapour of those elements.

The phenomenon of absorption can therefore be utilized for the identification of this series. From all this it will be seen that there is a profound and intrinsic link between the optical properties and the structure of the atom of an element. A careful study of these properties of the vapours of the elements, especially absorption, refraction and dispersion, will therefore be an important step towards the exploration of the structure of the atom. The researches described in this thesis were undertaken in the physical laboratories of the Maharajah's College, Vizianagram, with a view to study the optical properties of potassium vapour.

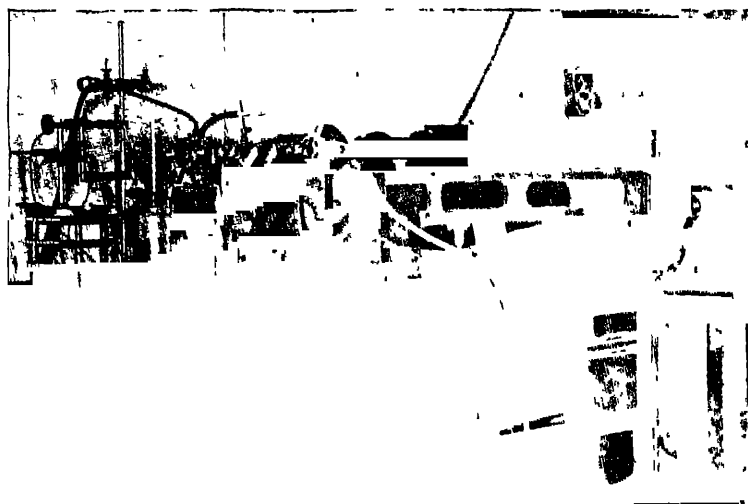
ABSORPTION IN THE VISIBLE AND THE ULTRA-VIOLET REGIONS.

A very complete study of the optical properties of sodium vapour was made by Professor Wood*, who has shown that the principal series is much more complete in the absorption than in the emission

* Wood *Phil Mag.*, 1908 and 1909; *Astro-physical Journal*, 1909.



FIG. I.



Apparatus as it stood in our study of the absorption of K-vapour.

spectrum, and has extended the series from the seven previously known to fifty-eight, the largest number observed for any element thus far. And the late Dr. P. V. Bevan* applied Wood's method to other alkali metals, and was able to extend the principal series. In view of the importance of obtaining accurate measurements of the lines of this series and a possible extension of the series, it was thought very desirable first to extend to the non-luminous potassium vapour, studies along the same line. Experiments were therefore undertaken to study the absorption of this vapour at different temperatures.

Experimental Arrangement.—The apparatus consists as shown in the photographic reproduction (Plate No. I) of a thin, seamless steel tubing about 30 inches long and 1 inch in diameter. The tube was furnished with two water boxes against the ends and two small lateral tubes were brazed into the steel wall, one at each end, for connexion with the pump and gas-generator. The ends were closed with two quartz plates cemented to the tube, with best sealing wax, and it was mounted in a metal frame on a stand provided with levelling screws, so that the tube could be conveniently placed with its axis parallel to that of the collimator of the quartz spectrograph. With the exception of a length of about 4" in the middle, the portion of the tube between the water boxes was covered with heating coils thoroughly wrapped with a number of layers of asbestos paper; and a continuous flow of cold water was maintained through the water boxes, throughout the experiment. The optical train of the quartz spectrograph used for the purpose consists of quartz lenses of 61 cm. focal length and a Cornu prism 41 mm. \times 65 mm. (long face), and the spectrograph is provided with a wave-length scale.

In this experiment a pretty large quantity of the fresh metal was cut into strips and introduced into the middle of the tube. By connecting the tube, through one of the side tubelures, to a gas-generator, pure, dry hydrogen gas was passed through the tube for some time, and thus the metal was kept in an atmosphere of hydrogen. With the metal in the centre of the tube, and the heating coils at the ends first raised to a high temperature, rapid distillation of the metal to the colder parts and the consequent deposition on the quartz windows could be prevented, and exposures of any length could be made under quite steady conditions.

Source of Light.—In these experiments a carbon arc was used as the source of light, since some of the emission lines in the arc serve as reference lines. The tube being mounted in position, light from the arc was concentrated by a quartz lens at the centre of the steel tube, and after emergence it was focussed by a sphero-cylindrical lens of quartz on the slit of the spectrograph. First the current in the heating coils was started, and a few minutes after that the tube was heated at the

* Bevan *Proc. Phy. Soc.*, 1909, and *Proc. Roy. Soc.*, 1910 and 1911.

centre by the flame of a Tecclue burner, which gave a high temperature. When the tube was heated first the absorption lines at the red end $1, s - 2, p'$, and $1, s - 2, p''$, made their appearance, and as the temperature was raised the accompanying channelled spectrum developed. With the increase of temperature and consequent increase of the density of the vapour, the higher members of the series also developed. When the temperature and the density of the vapour were sufficiently high to bring out the higher members of the series, it was found that the first three pairs of the series were immersed, so to speak, in a band spectrum, the cause of which will be explained later. Experiments were made when the tube was filled with hydrogen, and when there was a vacuum, the residual gas being hydrogen. With the tube at a temperature of 750°C nearly, and with exposures of $1\frac{1}{2}$ to 2 hours the principal series could be extended to 30. In the course of these experiments, when the temperature was raised still further, some traces of absorption were noticed in the subordinate series as will be explained later.

Continuous Absorption.—In this connexion it is very interesting to note that at high temperatures, the vapour, in addition to the absorption corresponding to lines of the principal series, exhibits what Prof. Bohr calls, "selective absorption in a continuous spectral region," beginning, as in Wood's experiments, on sodium vapour at the limit of this series, and extending into the ultra-violet. This confirms in a striking manner the theory that the absorption of the lines of the principal series results in final states of the atom in which one of the electrons revolves in larger and larger orbits. For, continuous absorption corresponds to transitions of the electron from the normal state to states in which it is in a position to remove itself infinitely far from the nucleus. And the electron in falling to the limiting orbit gives rise to a continuous spectrum, lying on the short wave-length side of the limiting line of the series. This phenomenon, as Bohr says, bears a complete analogy with the photo-electric effect from an illuminated metal plate where, by using radiation of a suitable wave-length, electrons of any velocity can be obtained. The frequency, however, should always lie above a certain limit connected, according to Einstein's theory, with the energy necessary to bring an electron out of the metal. For, according to the fundamental law of photo-electricity first suggested by Einstein,

$$\frac{1}{2} m v^2 = h \nu - w_0 = h (\nu - \nu_0)$$

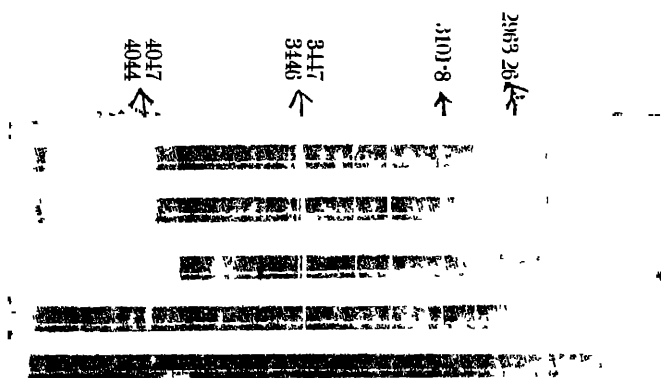
where ' h ' is the Planck constant ;

' v ' is the velocity of electron ;

' ν ' is the frequency of the incident light ;

and " w_0 " is the work done when an electron escapes from the atom to which it is attached and is equal to $h \nu_0$ where ν_0 is the characteristic frequency of the metal, on which the radiation falls. The frequency of the incident radiation should be above a certain limit, viz., ν_0 .

FIG 1-A



Principal Series.—For photographing the spectrum, Schumann plates and Wratten and Wainwright Allochrome plates, evenly sensitive up to 56μ were used.

When these experiments were in progress, S. Datta (now of the Presidency College, Calcutta) studied the absorption spectrum of potassium vapour at the Imperial College, London, in connexion with his investigation of the vacuum arc spectrum of potassium (*Roy. Soc. Proc. A*, Vol. 99, p. 69, 1921). He used a 10 ft. concave grating and extended the series in absorption to 42 (*Proc. Roy. Soc. A.*, Vol. 101, p. 540, 1922). But the scope of the present work is wider than Datta's. In the paper above referred to, Datta calculated by Nicholson's method the value of A , the limit of the series, by considering some of the lines beyond $m=9$ and obtained with this limit a formula which represents the whole series $(1,s) - (m,p)$ of potassium very closely, namely, $p_1(m) = 35008.480 - 109736.1 \left(m + 1.29667 - \frac{0.06154}{m} \right)^2$.

As in Datta's experiments, measurements were made on the photographs taken in the second order spectrum of the 10 ft. concave grating, giving a dispersion of about 2.8 A.U. per millimetre, by superior instrumental means, wave-lengths and wave-numbers given by Datta are used by the author for the 30 lines observed in these experiments, and these values are given in the second and the third columns of Table I, given below, from $m=10$ to $m=29$. In the fourth column, Bevan's values are given, and in the fifth column are given the differences between the values of ν observed and those calculated from the above formula.

TABLE NO. I.

m.	λ (Inter.)	ν (Vac.)	λ Bevan (Int.)	ν (observed) - ν (calculated from Datta's formula).
10	2927.602	34147.68	2927.9	.04
11	2916.114	34282.20	2916.5	.11
12	2907.203	34387.28	2907.5	-.05
13	2900.126	34471.18	2900.3	-.06
14	2894.407	34539.29	2894.5	.06
15	2889.788	34595.09	2889.6	.01
16	2885.857	34641.62	2885.8	.10
17	2882.614	34680.60	2882.8	.06
18	2879.864	34713.70	2880.2	.04
19	2877.509	34742.11	2877.8	.08
20	2875.494	34766.46	2875.7	-.01
21	2873.743	34787.64	2874.0	-.04
22	2872.214	34808.15	2872.4	-.06
23	2870.865	34822.51	2871.0	-.03
24	2869.668	34837.05	2869.9	.09
25	2868.627	34849.8003
26	2867.676	34861.24	.	.06
27	2866.832	34871.50	.	.10
28	2866.075	34880.7211
29	2865.407	34888.84	...	-.05

THE RED-CHANNELLED SPECTRUM.

In the red-channelled spectrum accompanying the first members of the series (1,s — m,p) the wave-lengths of 15 bands were measured by a Hilger wave-length spectrometer, which are clearly seen in the photographic reproduction (Plate No. II). This spectrum was studied by Roscoe and Schuster (*Proc Roy Soc.* XXII, p 362) and by Wood and Carter (*Phys. Rev.* XXVII, p. 113, 1908). The wave-lengths of these bands are given in the following table.—

For photographing the spectrum, Ilford "Special Rapid Panchromatic" plates were used.

TABLE NO. II.

No.	Wave-length	Wave-number
1	6811.0	14679 1
2	6760.0	14788.8
3	6711.0	14899 2
4	6661 0	15018.9
5	6622.0	15099.4
6	6584 0	15191 0
7	6544.1	15230.5
8	6506 0	15371.0
9	6488 5	15424.5
10	6443.0	15519.5
11	6412.0	15601.0
12	6388.8	15647.0
13	6366.1	15715.2
14	6332.2	15797.8

SATELLITES ACCOMPANYING THE MEMBERS OF THE PRINCIPAL SERIES.

In these experiments, besides the lines of the principal series, new lines which do not correspond to the emission lines of potassium were observed at high temperatures. These new lines, which are simply satellites clustered together within a small compass about the principal line which is the strongest of the assemblage, become, with the increase of vapour density, larger in number and more and more diffuse until at last they coalesce together with the principal line to form a thick band.

Fig. II,
Channelled spectrum

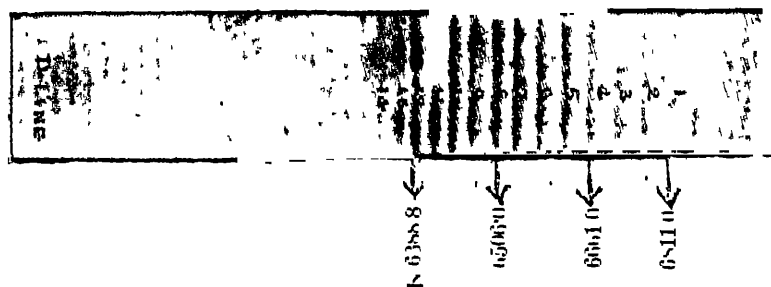


Fig. III

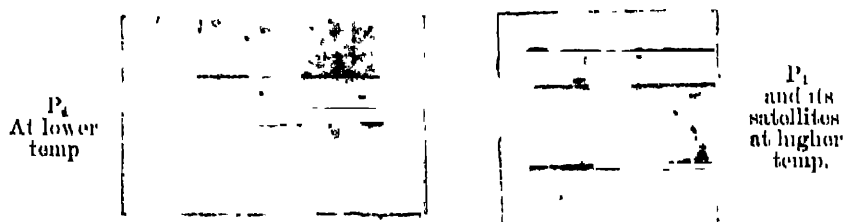
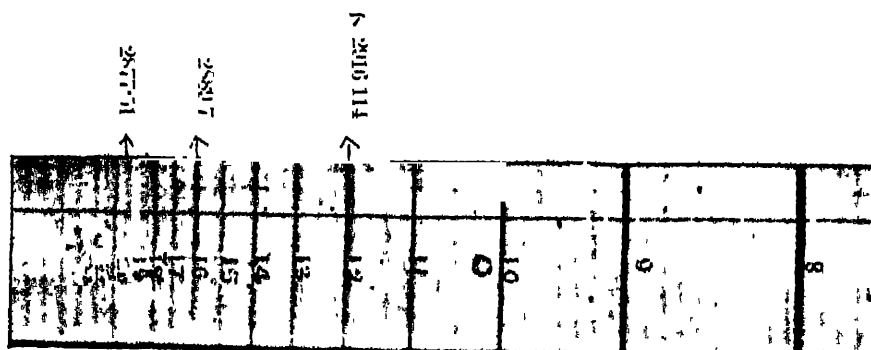


Fig. IV-A.





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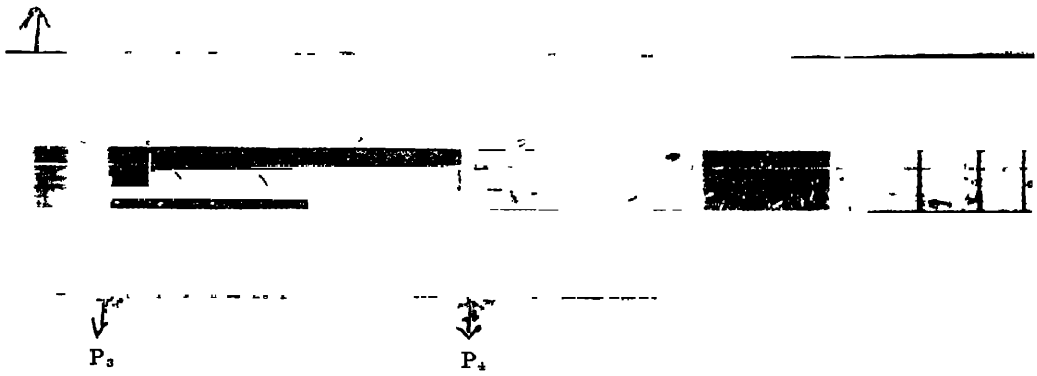
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FIG 1V.



By gradually increasing the density of the vapour and by photographing the absorption spectrum at different stages it is possible to recognize these lines. The wave-lengths of these lines along with their wave-numbers are given in the following table :—

TABLE NO. III

—	Line	Satellite	Wave-number
P ₃	4047.2	4119.1*	24280
	4044.15	4025.3†	24849
P ₄	3446.72	3434.6	29114
	3147.7	3461.65	28883
		3468.45*	28830
		3482.15*	28719
P ₅	3217.658	3221.6	31044
	3217.17	3223.36	31027
		3214.00*	31100
P ₆	3102.00	3100.00	32250
	3101.8	3103.5	32225
P ₇	3034.8	3033.15	32967
		3036.55*	32925
P ₈	2992.2	2990.34	33436
		2994.05*	33391

It will be seen from the photographic reproduction of the line 1,s — 4,p (Plate No. III) that fresh lines make their appearance at higher pressures and that they become more and more diffuse. The line 4119.1 I.A. was for the first time observed by Datta, as a faint emission line in his experiments with Lord Rayleigh's vapour lamp, and it is included by Fowler among the unclassified lines. It is for the first time reversed by the author in the course of these experiments, as seen in the photographic reproduction (Plate No. IV). The fact that this is also reversed with all those lines, one of whose terms is 1,s, shows that this is probably a combination line with 1,s as one of its terms. Attempts to classify this line were not successful, but the author opines that it is probably the combination line 1,s — 3,f.

Absorption of 1,s — 3,d.

In the course of these experiments it was found that at about 700° C. this combination pair was absorbed, *as was also observed by Datta independently*. When examined by the wave-length spectrometer this was found to be a sharp and well-defined line, but when analysed by a reflection grating containing 30,000 lines, it was found to be a pair, the wave-lengths of which, as measured in the second order spectrum, are

* Not recorded by Datta, who simultaneously with the author studied the phenomenon.

† The remaining lines merged into the thick band.

4642'18 and 4641'59. This was pointed out by the author in a short note in *Nature*, August 19, 1922. The absorption of this pair is considered very important, *as pointed out by Datta, and independently by the author* in a note that appeared in the April number of the *Astro-physical Journal* on "The absorption of potassium vapour at high temperatures, and its bearing on the selection principle of quantum theory," as it is a direct negation of the principle in its present form. For, according to the Bohr-Sommerfeld theory of spectral emission, the spectral lines are emitted as the electron changes its habitat from one orbit to another of less energy, the rotational quantum number corresponding to the initial and final orbits changing only by 1, 0, or -1. These lines represent an inter-orbital transition requiring a change of two units in the quantum number which is not allowable according to the selection principle. The presence of this line strongly supports the views advanced by Messrs. Foote, Mohler, and Meggers, in a short note on the "Significant exception to the principle of selection" (*Phil. Mag.*, April 1922) in which the authors found 1,s — 3,d, as the strongest pair in the *emission* spectrum, even when the applied electrostatic field exerted no influence on the radiation. This absorption experiment, together with the experiments of the foregoing authors, seems to prove conclusively that the method whereby the rotational quantum numbers have been assigned, requires reconsideration. The absorption of this pair is important in more than one way. For, as pointed out by Fowler, *Report on Series in line Spectra*, page 101, it suggests the presence of a satellite in the members of the diffuse series, and suggests also that the Bergmann series (3,d — 4,f) should consist of doublets with a constant separation corresponding to the two limits given by 3,d, and 3,d'.

$$f' (m) = 3,d - m,f.$$

$$f'' (m) = 3,d' - m,f.$$

Since there are two values of 'd', falls from the (f) orbits to 3,d, orbits yield doublets in this series.

This opens up a new field of research, for, by a large concave grating spectrograph, and by using plates sensitized with pinacyanol, and dicyanin, to the infra-red, the region containing the lines of this series can be photographed and their structure can be studied. But as the lines of this series as found in the ordinary arc are diffuse on the red side, for accurate wave-length measurements it is essential to use either a

Since this thesis was written, further experiments were made by the author with sodium and lithium, where by using a long column of vapour under purely thermal excitation, the author obtained 1,s — 3,d lines as absorption lines, while Dr Datta obtained similar lines in the case of *Rb* and *Cs*. These experiments confirm the view that probably the "Selection Principle" does not hold good in the case of absorption as in the case of electronic collisions.

FIG. V-3.

1,8 - 3,4

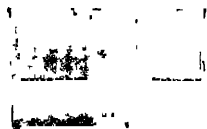
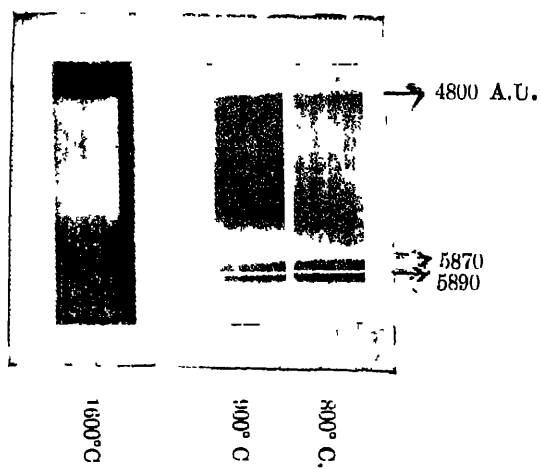
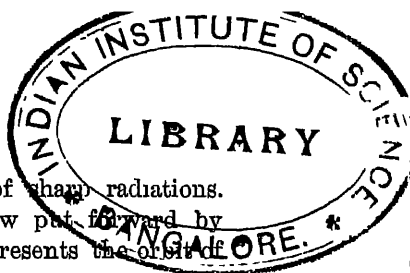




Fig V





vacuum arc or electrodeless discharge as a source of sharp radiations. Lastly, the absorption of this pair confirms the view put forward by Bohr that the $1,s$ orbit is very significant as it represents the orbit of the electron in the normal state of the atom.

To find if this pair exhibits anomalous dispersion, the horizontal fringe system obtained by the interferometer was received on the vertical slit of the wave-length spectrometer, the tube containing the vapour and the compensating tube being closed with plane parallel plates of glass, and it was found that there was not even the slightest trace of anomalous dispersion.

ABSORPTION AT HIGH TEMPERATURES.

As it was found that there were slight traces of absorption in the associated series of the element at the highest temperature used in the experiments, another series of experiments was instituted with a view to find if the associated series would be absorbed. The behaviour of the vapour at these high temperatures was very remarkable. As the temperature was gradually raised from 750°C. , the band 5780 A.U. (possibly $2,p - 4,s$) gradually extended towards the short wave-length side. At about 900°C. when the band did not extend far towards the violet, a channelled space appeared between this and the red-channelled spectrum accompanying the first pair of the principal series. As the temperature was raised this diffuse band became wider and wider till at the highest temperature used, about 1000°C. , it extended from 5870 to 5350 A.U. Meanwhile the absorption at the violet end increased and extended finally up to 4800 A.U. , the transparent region at this temperature being only about 550 A.U. Plate No. V* shows the diffuse and broad band at 5780 A.U. and the narrow transparent region between this and the violet band. This region, at the highest of the temperatures used by the author, was filled with a host of dark bands and lines, some of them being diffuse and abnormally faint. As has been pointed out by the author in *Nature*, August 19, 1922, at these high temperatures the chemical difficulties are so great and the conditions in the experimental tube so unstable, that it was found difficult to obtain a good photograph, on account of the tube giving way, possibly owing to the action of potassium vapour on the walls of the tube at these high temperatures.

Experiments were made both when the tube was filled with hydrogen and when there was a vacuum, and it was found that the phenomenon was best seen when there was a vacuum, though at the same time the difficulties due to the rapid distillation of the metal to the colder

* The dark line in the middle of the narrow region of transmission, to the left of this plate, is the D line due to traces of sodium in the potassium used in these experiments.

parts increased. And the following are the more prominent of the bands and lines as measured by the wave-length spectrometer :—

5780—5350 thick band, sharp on the red side and diffuse on the violet side.

5340	}	diffuse and broad.
5300					
5205					
5100					
4900					
4870					
4831]				

The bands 5780, 5340 and 5100 seem to correspond to 5782, 5340, 5323 and 5100 of 1,p — m,s of potassium. The line 4831 is well defined and in intensity comes next to 4641 and 4642. This is undoubtedly the same as the *emission* line observed by Robertson in his experiments on the electrodeless discharge in potassium vapour. (*Phys. Rev.*, May 1922.) As a result of his attempts to correlate the line, the author opines that this is the combination line 1,p — 8,p

λ Observed.	ν Observed.	ν Calculated.
4831	20699.5	20694.3
		(21963.06 — 1268.8)

and it is very significant that one of its terms is 1,p, as it appears only at high temperatures, along with 1,p — m,s lines.

STRUCTURE OF 4641-42 OF POTASSIUM.

If we accept the fact that potassium is a mixture of two isotopes, as recently shown by Aston*, we might expect each line of a doublet of the potassium spectrum to be made up of two components. For, according to Bohr's theory of spectral lines, we know that

$$\nu = \frac{2\pi^2 N^2 e^4}{c h^3} \cdot \frac{mM}{M+m} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where ν is the frequency of the radiation ;

Ne is the charge on the nucleus ;

M is the mass of the nucleus ;

e & m are charge and mass of electron ,

c is the velocity of light ;

h is the Planck universal constant of radiation ; and n_1 and n_2 are integers (for H).

* *Nature* 107, p. 72, March 17, 1921, and *Phil. Mag.*, S VI, Vol. 42, No. 249, September 1921, p. 436.

By the use of the Mass Spectrograph (*Phil. Mag.*, April 1920, p. 449, and May 1920, p. 611) where he devised a very ingenious method of focussing positive rays, Dr. Aston has shown that a large number of elements are complexes consisting of two or more kinds of atoms, having identical chemical properties but differing in atomic weight by one or more units.

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FIG. VI.

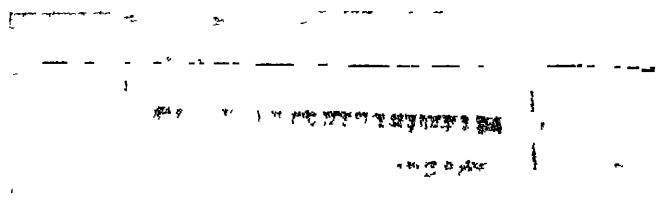


FIG. VII.



Applying this formula for the difference between the series spectra of the isotopes of potassium we get for the two isotopes the frequency relation

$$\nu_1 - \nu_2 : M_1 / (M_1 + m) - M_2 / (M_2 + m)$$

where M_1 , M_2 , and m are respectively the masses of the nuclei of the isotopes, and of the electron ;

$$\text{and } M_2 = 39 \times 1.649 \times (10)^{-24} \text{ gm.}$$

$$M_1 = 41 \times 1.649 \times (10)^{-24} \text{ ,,}$$

$$m = 0.899 \times (10)^{-27} \text{ ,,}$$

Therefore $\frac{\Delta\lambda}{\lambda} = m (M_1 - M_2) / M_2 (M_1 + m)$ which gives a separation of the components .002902 A.U

While according to the view put forward by Professor McLennan (*Proc. Roy. Soc.*, A. 711, Vol 101, p. 340) from his experiments on the structure of line 6708 of the isotopes of lithium, the observable spectral displacement for isotopes is equal to the atomic number multiplied by the displacement calculated on the Bohr theory, the separation of the components being $(19 \times .002902)$ or 0.055138 A.U. In this connexion, it is interesting to note that Nicholson (*Nature* 110, p. 37, July 8, 1922) doubts the fact that McLennan's new series is the spectrum of an isotope, and is of opinion that it is the principal spark line of lithium which has a value very close to 6708 A.U. It is therefore worthwhile to examine the structure of some of the potassium lines. For this purpose, on account of the sharply defined nature of the pair 1,s — 3,d in the absorption spectrum, and on account of the interest that centres round this, it was proposed to study the structure of this line with a sufficiently high resolving power optical instrument.

Experimental Arrangement.—The discharge tube consists of a glazed porcelain tubing* about 50 cm. long which was fitted with two brass fittings cemented to the tube at the two ends with best sealing wax. Each of these contained, as will be seen from the photographic reproduction (Plate No. VI), a water box for constant circulation of water and a side tubelure. These were provided at the ends with plane plate-glass windows and the discharge passed between two cylindrical electrodes of platinum (Plate No. VII). The tube was wrapped with a heating coil thoroughly covered with some layers of asbestos paper by which the temperature could be maintained uniform. By means of an automatic Sprengel pump, made for the purpose, the tube was exhausted to a pressure of the order of 0.001 mm. and the interposition of a long phosphorous pentoxide tube between the pump and the discharge tube was found

* This tube was kindly lent to the writer by Mr V Appa Rao, Professor of Physics, Government Arts College, Rajahmundry, to whom his best thanks are due.

to suppress the mercury lines effectively. And under this high vacuum, pure potassium vapour was distilled into the discharge tube from the other side tubelure. When the tube was maintained at about 350°C . and when an intense discharge was passed through the tube, it was found that 1, s — 3, d pair came out with moderate intensity. The discharge was maintained by a $10''$ induction coil operated with an auto-mercury interrupter, on a current of 18 to 20 amps. For examining the structure, a Lummer Gehroke plate of glass was used to effect the resolution, and the diffraction pattern was examined.

Data for Lummer Plate--

$$d = .468 \text{ cm.}$$

$$h = 22800.$$

$$\lambda = 4641 \text{ A.U.}$$

$$\mu = 1.5179.$$

$$\frac{d\mu}{d\lambda} = - .940.$$

$$\text{R.P. at } 4641 \text{ is } 340,000$$

$$d\lambda_{\max} = 204 \text{ A.U.}$$

The plate was provided with a right-angled prism with one acute angle equal to 22° .

Theory of the Lummer Plate--

In the case of the Lummer plate, the order of the spectrum h is given by $h = \frac{2d\sqrt{\mu^2 - \sin^2 i}}{\lambda}$ (1)

where 'i' is the angle of exit ;

'd' is the thickness of the plate.

If the exit of light is grazing $h = 2d\sqrt{\mu^2 - 1}/\lambda$

If we differentiate this with respect to λ , we get

$$h^2 \lambda = 4d^2 \left(\mu \frac{d\mu}{d\lambda} - \frac{\sin 2i}{2} \frac{di}{d\lambda} \right) \quad (2)$$

since 'h' is very large, we get the equation

$$h \lambda^2 \Delta h = - 2 d^2 \sin 2 i \Delta i$$

Therefore from equation (2) we get the approximate relation

$$2 d^2 \sin 2 i \Delta i = \left(h^2 \lambda - 4d^2 \mu \frac{d\mu}{d\lambda} \right) \Delta \lambda$$

if we put $\Delta h = 1$

$$\Delta \lambda = d \lambda_{\max}$$

$$\therefore d \lambda_{\max} = - \frac{\lambda^2}{h \lambda - \frac{4 d^2}{h} \mu \frac{d\mu}{d\lambda}}$$

■

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FIG. X



Thus 'h' & $d \lambda_{\max}$ are calculable for any wave-length (λ) when 'd' the thickness, μ and $\frac{d\mu}{d\lambda}$ are known. In order to avoid the necessity of knowing the order of the diffraction pattern, the formula used in this experiment for measuring up the fringe pattern was the same as that used by McLennan.

$$\Delta\lambda = \frac{a_s^2 - a_m^2}{a_{m_2}^2 - a_{m_1}^2} \cdot d \lambda_{\max}$$

where the denominator is the difference between the squares of the distances of two consecutive main line fringes from the central line of the pattern

' a_m ' is the distance of the main line fringe from the central line of the pattern; ' a_s ' is the distance from the central line of a satellite fringe of the same order; $d \lambda_m$ is change in λ causing fringe of the m th order of the system of fringes due to $(\lambda + d \lambda_m)$ to coincide with fringe of $(m+1)$ th order of λ .

As the high resolving power accessories are only suitable for observation of rays of a considerable degree of homogeneity it is very necessary to isolate the radiation under test, from its neighbours. Therefore, in these experiments light from the discharge tube was first concentrated, as shown in the diagram (Plate No VIII), by a sphero-cylindrical lens of glass on the collimator slit of the wave-length spectrometer, the eyepiece attached to the telescope of which was removed, and another Hilger spectrometer was mounted with its collimator in train with the telescope of the previous one and the line under investigation was made to fall on the slit of the second instrument, a Nicol prism with its short diagonal horizontal being interposed in front of the slit of the second instrument, the function of the Nicol being to polarize light in such a plane that it is copiously reflected at the inner surface of the plate. On the table of this second instrument the Lummer plate was mounted with its plane vertical so as to get the fringe pattern on both sides. Photographs of the fringe pattern were taken with a camera lens of 21" focal length by using Wratten and Wainwright Allochrome plates. It will be seen from the diffraction pattern of the Lummer plate (Plate No. X) that there are no satellites. But the diffuse nature of the lines shows that with an instrument of a high resolving power each of the bands divides possibly into two lines, one being a faint line, in which case the separation of the components will probably be in accordance with Bohr's theory, or at any rate it cannot be in accordance with McLennan's views. For, if there are components with separation = 0.55138 A.U. (according to McLennan's views) they must be easily detectable by the Lummer plate used in this experiment.

INFRA-RED EMISSION AND ABSORPTION OF POTASSIUM.

In spite of the excellent and more recent investigations the whole matter of the origin of spectral lines seems to be in a state of confusion, as can be readily seen from the conflicting views advanced by Saha, Hemsalech, Seeliger, etc. For Saha* published a series of papers on the theory of thermal ionization and thermal radiation of gaseous elements and proposed a physical theory of stellar spectra, where the author discussed the problem of atomic dissociation from the thermodynamic standpoint. By means of Nernst's heat theorem, and the equation of the "reaction isobar," Saha calculated the degree of ionization for a number of elements at different temperatures and under different pressures from which he attempted to find to what extent atomic dissociation into positively charged atom and electrons was possible in the sun and different stars. Eddington,† while dealing with the roll of radiation pressure in the constitution of stars, incidentally suggested that elements may be ionized owing to high temperatures. This fact was also independently suggested by Jeans.‡ According to the views advanced by these authors, the energy necessary for excitation of the spectral lines of an element is in the order principal series; diffuse series, sharp series, Bergmann series, etc. Hemsalech,§ from a series of investigations, has reached conclusions which differ materially from the views advanced by the foregoing authors. He thinks that the emission of spark lines is connected with the existence of strong electric fields, and is further of opinion that King's tube-resistance furnace spectra are not of a purely thermal origin. While Messrs. Seeliger|| and Thaer investigated the arc and spark spectra of the alkalis where it was shown that the energy necessary for excitation of the arc lines of an element is in the order Bergmann series; principal series; diffuse series; sharp series; etc., and they add that it is significant that in its entire behaviour the Bergmann series, of the whole arc series, is farthest removed from the spark series. Thus the lines of Bergmann series, according to Seeliger, are associated with the normal atom of the element. As regards the question of the reversal of lines, at low temperatures, only the lines corresponding to the combination $1,s - m,p$ are absorbed, while the lines belonging to the diffuse series, Bergmann

* M. N. Saha "Ionization in the Solar Chromosphere" (A), *Phil. Mag.*, October 1920, "Elements in the Sun" (B), December 1920, "On the Temperature Radiation of Gases" (C), February, 1921.

† Eddington. *M.N.R.A.S.*, Vol 77, pp 16 and 596, Vol 79, p. 2, *Observatory* No 557, pp. 341-358, October 1920.

‡ Jeans *M.N.R.A.S.*, Vol 79, p 319.

§ Hemsalech *Comptes Rendus* 169, pp 915-918, Nov 17, 1919.

Do 169, pp 1034-36, December 1, 1919.

Do. 170, pp 31-38, January 5, 1920.

Science Abstracts, Section A, 1921, December, 1921.

Do. do 130, do. 1922.

Phil. Mag., February, 1922.

|| Seeliger and Thaer. *Ann d Phys* 1921, IV, 65, pp. 423-448.

series, etc., would be absorbed at higher temperatures, or under electrical stimulus. But according to Seoliger's views, the temperature necessary for the reversal of the lines of different series increases in the order Bergmann series, principal series; etc., thereby showing that the lines of the Bergmann series should be absorbed before the absorption of the principal series begins. If, therefore, in an absorption experiment it can be shown that the Bergmann lines would be first absorbed, we shall have to revise a good deal of our views regarding atomic structure and the origin of the spectral lines. The subject of infra-red absorption has therefore an important bearing on the question of temperature radiation and the origin of spectral lines. It is therefore necessary by studying the absorption spectra of the alkali metals, to ascertain as fully as possible the frequencies which are associated with the atom of the element in definite physical states, especially in the infra-red region. Perhaps on account of the difficult technique, the spectroscopic study of the transparency of the vapours of the alkali metals to heat waves has been left in the background. The main purpose of this investigation is therefore to study the absorption of potassium vapour in the infra-red region and to find if Bergmann lines would be absorbed and, if so, at what temperature.

With a view to proceeding in this direction some preliminary experiments were made by the author on the emission lines, in the spectrum of potassium vapour in the same region. This was previously investigated by Becquerel, Snow, Coblentz, Paschen, Moll, Bergmann, etc. Most notable among these were the experiments of Coblentz,* who worked with a rock-salt prism and a radiometer; W. J. H. Moll † examined the emission spectrum, using for the purpose a rock-salt prism, a thermopile, and an automatic device for recording the galvanometer deflections. With the automatic device he was able to explore the region beyond 2μ more thoroughly than was possible by making personal observations. Some time later, Paschen ‡ investigated the same problem with a concave grating and a linear thermopile, while Bergmann § investigated by the photographic method. Although with the rock-salt prism spectrometer such a high dispersion as in Paschen's investigation cannot be obtained, with the linear thermopiles of the most sensitive type recently made by Adam Hilger, Ltd., and the highly delicate Paschen galvanometer made by the C.S.I. Co. it seemed to justify another attempt to study the emission of potassium vapour in the infra-red.

Experimental Arrangement.—For studying the emission spectrum, in some experiments pure potassium chloride, previously well dried and powdered, was used in the carbon arc, using for the purpose hollowed-out carbon electrodes filled with the salt, and a direct current of 12 to

* Coblentz *Supplementary Investigations of Infra-red Spectra*, 1908

† W. J. H. Moll *Proc. Amsterdam Acad.*, pp. 544—548, 1907.

‡ Paschen : *Ann. de Physic*, 27, pp. 537—570, 1908.

Do, 717—738, 1910

§ Bergmann. *Wiss. Photogr.* 25, pp. 113—145, 1908.

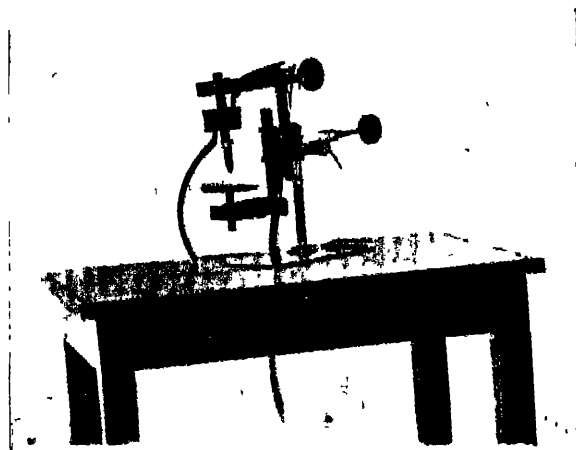
15 amps. was used for the purpose. Subsequently it was found convenient to use small lumps of the metal itself in a type of the carbon arc modified by the author (Plate No. XI). A slightly different form of this arc was used by Hemsalech and the Comte de Gramont in their investigations on the arc and spark lines. This type was found to be specially serviceable in studying the spectra of metals having low boiling points. As is seen from the photographic reproduction, the upper carbon is surrounded with a water box through which there was a constant circulation of cold water, thereby preventing the temperature of the electrode from becoming very high; and the lower electrode consists of a copper plate 8 cm. in diameter with a small depression in the middle to contain the metal or the salt in question. The whole arrangement was found to be so satisfactory that much larger galvanometer deflections could be obtained than by the first method.

The rock-salt spectrometer and the linear thermopile used in these experiments were made by Adam Hilger Co., a diagram of which is given at the end. It was of the constant deviation type, with Wadsworth mirror prism combination. The instrument was furnished with two symmetrical slits, each having an effective length of jaw of 20 mm. Light entering from the first slit S' is collimated by a nickel-steel concave mirror M' and then passes through the rock-salt prism (32 mm. \times 42 mm.) to a nickel-steel plane mirror M'' , from which it is reflected to the second concave mirror by which an image of the spectrum is depicted on the second slit just behind which there is the linear thermopile. The entire thermopile was protected from extraneous radiation by a nickel-plated case. The helical drum, by the rotation of which different parts of the spectrum can be brought into coincidence with the linear thermopile, was calibrated in wave-lengths from $.5\mu$ to 9μ . Energy measurements were made by the linear thermopile in conjunction with a Paschen galvanometer made by the C S I Co.

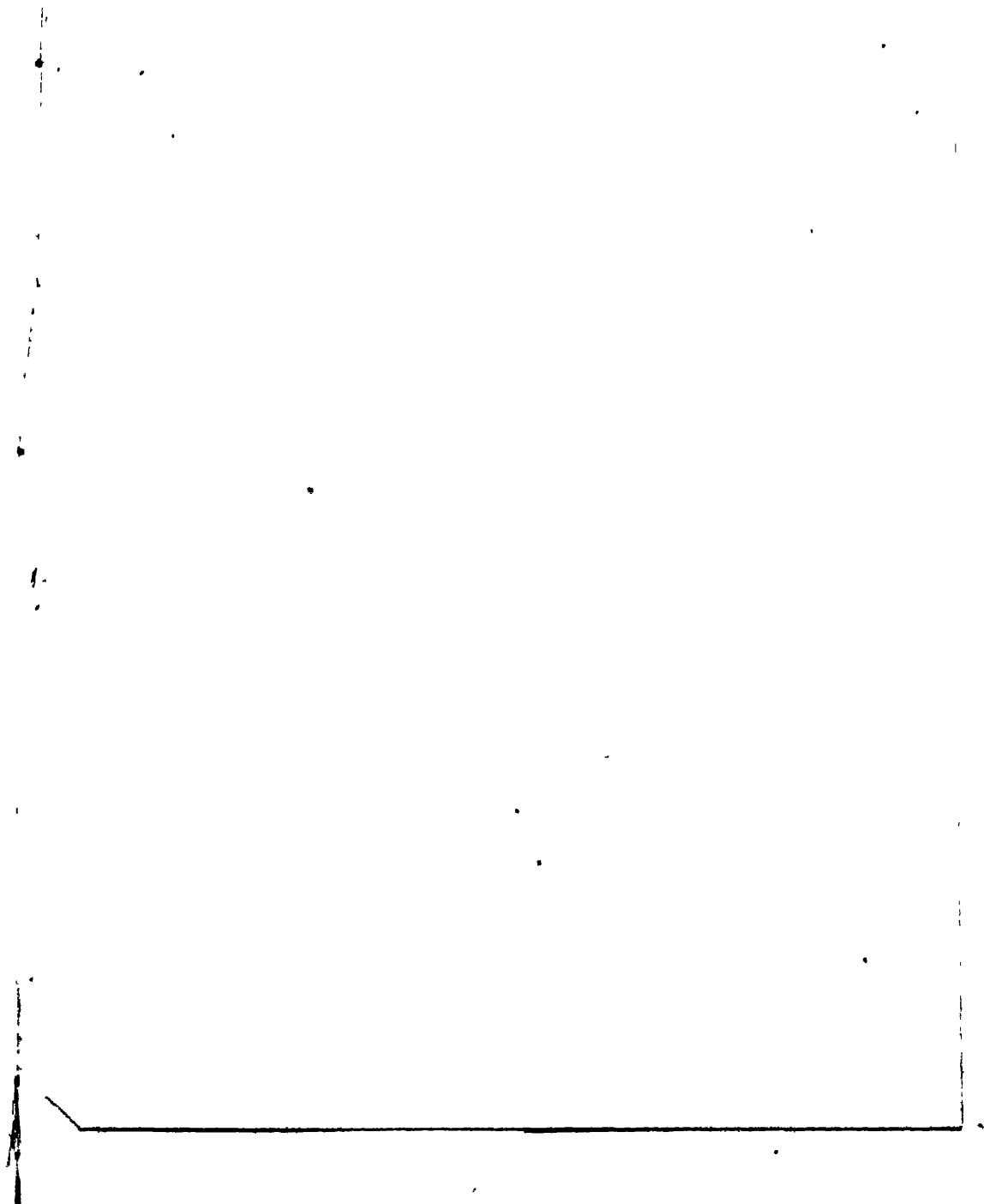
Paschen Galvanometer.—The magnet system consists of two groups of 13 magnets each, the magnets being arranged alternately on opposite sides of a fine glass stem which supports also a very thin glass mirror. The whole moving system of this galvanometer weighs about 28 to 30 m.gm. A special feature of the instrument is the winding of the coils which are graded so as to have the best cross section. The coils are elliptical in shape and are wound in such a way as to obtain the maximum field for the given resistance. The galvanometer is extremely sensitive to temperature changes. In order to obviate this difficulty the instrument was covered with a thick layer of absorbent cotton all round.

Thermopile.—In this linear thermopile the Hutchins alloys (Bismuth-tin, and Bismuth-antimony) were used, and it is found that this has a sensitiveness nearly 50% greater than the previous model, and is almost entirely free from creep. The dimensions of the sensitive area are 20 mm. \times 1.6 mm. The number of junctions is 20, and the resistance is 12 ohms, approximately.

FIG. XI







The period of the galvanometer in field was 6.5 seconds nearly, the coils being connected in series. The deflection at 1 metre distance for one micro-ampere was about 360 cm. With the four coils in series, the resistance was 12 ohms.

Before the nickel-plated case was screwed in position, the thermopile was removed, and the eye-piece, which is attached behind the slit S'', was mounted in position, and sunlight was directed on to the slit of the spectrometer by means of a heliostat, and the solar spectrum was obtained. The eye-piece was focussed on the Fraunhofer lines, and the slit width was adjusted to obtain very sharp lines. Then the prism was adjusted so that the radiation at S'' was in agreement with the reading on the wave-length drum. In this way, settings were made for B, D, E, and F lines of the solar spectrum. The instrument was similarly standardized in the long wave region by means of the absorption bands of water, using for the purpose a layer of water of .5 to 1 mm. in thickness, so that the bands are sharp and well defined. Having thus standardized the instrument, the eye-piece was removed, the thermopile placed in position, and the nickel-plated case was screwed in its place.

To avoid stray air currents and consequent changes in temperature, the whole spectrometer was enclosed, as will be seen from the diagrammatic plan (Plate No. XII), in a box furnished with two windows, one in front of the collimator slit and the other near the wave-length drum. The box was painted inside with black varnish, and outside with white enamel. The outside of the box was further covered with a layer of asbestos cloth, and the space inside with layers of cotton wool. To keep the air surrounding the rock-salt prism free from aqueous vapour, dishes containing fused calcium chloride and phosphoric anhydride were placed round the spectrometer.

In the first stages of the work, in spite of these precautions very great difficulty was experienced in making energy measurements owing to want of steadiness in the zero of the galvanometer. Sometimes though there was absolutely no radiation falling on the slit of the spectrometer, the spot of light used to oscillate over a range of 4 to 5 cm., even these oscillations being quite irregular and sudden. It was subsequently found that the hot summer winds were the cause of these sudden fluctuations in the zero of the galvanometer; and to overcome these difficulties it was found necessary to work in the early hours of the morning from 4 to 8, when there was a perfectly calm and cool atmosphere. Under these conditions it was found that the zero of the galvanometer was perfectly constant even though the full scale deflections were obtained on certain occasions. In investigating the emission spectrum, quite a large number of readings were taken to establish the exact position of the maxima. The wave-lengths of the lines found in this investigation are given in the following Table No. IV, along with the lines found by other investigators.

TABLE NO. IV.

 λ . A.U.

Author.	Paschen	Moll.	Bergmann
36700	...	40400	
		37300	
30600		31400	31800
		27600	
27150	{ 27215	.	.
	{ 27065	.	.
15280	15165	15300	15282
12500	12523	12500	12507
	12434	..	12415
11900	...		
11750	11771	11800	11762
11600	11689		11678
11000	11028	11100	11012
10800	..		
9620	..	9700	9590
..	...		8908
.		...	8500

Discussion of Results.—From a comparison of these values it will be seen that the values given by Moll are consistently slightly higher than the values of the author, which is probably due to the method adopted by Moll for automatically recording the galvanometer deflections. The line $1'19\mu$ corresponding to which there is none in the observation of the other investigators is probably a new one. The line $3'67\mu$ is obviously the combination line $2,p-3,s$, being the same as the line $3'7\mu$ found by Moll, but not recognized by the later investigators. The line $2'72\mu$ is the combination line $2,s-3,p$ and corresponds to $2'72\mu$ & $2'71\mu$ found by Paschen by the concave grating. The lines $1'175\mu$ and $1'25\mu$ are the first members of the diffuse and the sharp series respectively.

Absorption in the Infra-red.—For studying the absorption in this region, the method adopted was essentially the same as that used by the author in his experiments on "The Absorption of Potassium Vapour in the Visible and Ultra-Violet." Only, instead of an arc lamp, a metal filament lamp was used as the source of light. And to protect the thermopile from extraneous radiation there were placed between the slit of the spectrometer and the source of light four co-axial cardboard diaphragms pierced with apertures about 1" in diameter. A pretty large quantity of the metal was enclosed in the steel tube which was then filled with pure dry hydrogen. After subjecting the tube to a preliminary heating up to about 350°C . the tube was connected to an air pump and was exhausted to .5 cm. When the tube cooled down to the room temperature, observations were made first on the emission spectrum of the metal filament lamp. Then the tube was heated and the enclosed metal was vaporized in the manner explained in the previous experiment, and observations were made of the transmission spectrum

at different temperatures, the maximum temperature used by the author being about 700°C . At higher temperatures it was found practically impossible to maintain the vapour at a constant density chiefly due to the distillation to colder parts. The galvanometer deflections which were proportional to the incident and transmitted energy are given in Table No. V, for two different temperatures, 500° and 650°C . roughly. At both these temperatures, as the galvanometer deflections for wave-lengths below 1μ were too small to be relied upon, they were not recorded. But as these experiments were mainly intended to find if Bergmann lines (1.517μ , 1.103μ ; $.96\mu$ and $.89\mu$) would be absorbed by the normal atom. in order to study the region 8μ to 1.2μ more thoroughly, energy measurements were made at a lower vapour density by reducing the temperature of the tube, the results of which are given in Table No. VI.

Incident and transmitted energy curves (Plates Nos. XIV and XV) were drawn by plotting the galvanometer deflections against wave-length values, from which it is clear that the vapour does not exercise any selective absorption in the infra-red region, at any rate below 600° or 650°C ., but that the absorption at $.77\mu$ (the first member of the principal series) extends gradually to the long wave-length side also with increase of temperature, as is clearly seen from the transmission percentage values calculated for temperature 500°C in Table No. V, and also for wave-lengths between $.77\mu$ and 1.2μ in Table No. VI. It is therefore beyond doubt that the lines of the principal series are the first to be absorbed as the temperature is gradually raised. In this connexion it is also interesting to note that as a result of experiments conducted by the author (described in the previous pages) at high temperatures with a view to study the absorption of the vapour, it was found that there were distinct traces of absorption in the diffuse series at about $1,000^{\circ}\text{C}$.

TABLE NO. V.

Wave-lengths. μ	Galvanometer deflections in cms.			Transmission percentage for 500
	Incident energy	Transmitted energy at 500.	Transmitted energy at 650.	
1.0	8.00	2.00	0.35	25.00
1.1	12.10	7.40	6.65	61.00
1.2	16.00	11.50	10.10	72.00
1.3	18.00	14.95	12.85	83.00
1.4	20.75	17.20	15.00	83.00
1.5	24.20	20.50	17.20	85.00
1.6	27.00	22.70	20.00	84.00
1.7	28.45	24.20	20.10	85.00
1.8	28.30	24.30	20.70	86.00
1.9	26.80	23.00	19.60	86.00
2.0	25.45	22.00	18.90	86.50
2.1	24.60	21.20	18.10	86.50
2.2	23.00	19.90	17.25	86.00
2.3	20.50	17.50	14.85	86.00
2.5	14.90	12.70	10.10	85.50
2.6	11.15	9.50	7.95	85.50
2.7	7.00	6.10	4.55	86.50
2.8	3.80	3.30	3.20	86.70
2.9	2.50	1.90	1.70	76.00
3.0	1.20	0.95	1.00	80.00

TABLE NO. VI

Wave-lengths. μ	Galvanometer deflections in cms		Transmission percentage
	Energy incident.	Energy transmitted.	
0.77	1.70	0.60	35.0
0.80	2.30	1.00	43.0
0.82	2.60	1.20	44.0
0.84	3.00	1.35	45.0
0.86	3.50	1.50	43.0
0.88	4.00	1.75	43.0
0.90	4.60	2.00	43.5
0.92	5.25	2.40	45.7
0.94	5.95	3.20	53.7
0.96	6.50	4.00	61.0
0.98	7.35	4.70	63.8
1.00	8.00	5.70	71.0
1.02	8.70	6.30	72.3
1.04	9.50	7.10	74.6
1.06	10.40	8.20	78.7
1.08	11.20	9.15	81.5
1.10	12.10	10.10	83.4
1.12	12.90	10.70	83.0
1.14	13.60	11.55	85.0
1.16	14.40	12.30	85.4
1.18	15.10	12.90	85.6
1.20	16.00	13.70	86.0

The thermopile, however thin it may be, usually occupies a few Angstrom units in the spectrum when it is made to pass through the whole range. When the absorption line is broad as in the case of the principal series, the junction may be completely covered by the line, and comparatively lesser deflection is obtained. But if we are dealing with a faint and narrow region of absorption, the junction covers not only this faint and narrow region of absorption but also the surrounding region of free transmission. Hence the effect of absorption may be completely lost when examined by the thermopile. It was therefore thought that the photographic method would be more decisive.

For photographing the spectrum in this region the plates were sensitized for the red and the infra-red region with pinacyanol according to a recipe given by Prof. W. J. Pope of the University of Cambridge :—

50 c.c. of distilled water.

25 c.c. of alcohol.

1 c.c. of 1 per cent alcoholic solution of pinacyanol.

A "Special Rapid" Ilford plate was bathed in such a solution, in absolute darkness for about three minutes, and then quickly dried before a table fan. With long exposures, the plates were found to be

sensitive up to $.9\mu$ though the sensitiveness diminishes rapidly from $.8\mu$. By using a reflection grating with 30,000 lines, the spectrum was photographed in the first order which shows no traces of absorption at $.89\mu$ and $.85\mu$ of the Bergmann series.

These experiments go to show conclusively that the temperature necessary for the reversal of lines of different series increases in the order : principal, diffuse, etc.

Electrically Luminiscent Potassium Vapour.—It has been pointed out in the previous pages that for the vapour of an element to absorb light corresponding to a given series in its spectrum, it is necessary that in the vapour there should be a fairly large number of atoms with orbits corresponding to the first term of the pulse of radiation to be absorbed, i.e., the atom should be in that one of the two states possessing the smaller energy value. For the lines, $2,p - 3,d$; $2,p - m,s$; or $3,d - 4,f$ to be absorbed it is necessary that there should be a sufficient number of atoms with $(2,p)$ or $(3,d)$ orbits. According to our ideas of the origin of spectral lines, energy necessary for the excitation of the lines of the Bergmann series is greater than that of the diffuse and the sharp series. The lines of the Bergmann series therefore begin to be absorbed at high temperatures, viz., at the temperature of emission of the sharp series. As it is very difficult to obtain the very high temperature necessary for the reversal of the lines of this series in the laboratory, except by King's tube-resistance furnace, it was thought convenient to adopt the alternative method of keeping the vapour in a feebly luminiscent state.

Experimental Arrangement.—The tube used for the purpose was exactly similar to the one used in the study of the line 4641—42 (Plate No. VI). The vapour of the metal was enclosed in the glazed porcelain tubing on which the heating coils were wound. For studying the absorption, the mirror spectrometer and the Paschen galvanometer described in detail in the previous pages were used, as all the lines of the Bergmann series are in the long-wave region. When the discharge tube was mounted before the slit of the spectrometer and the discharge from a small induction coil was passed through the vapour, it was found that the galvanometer was seriously affected by the presence of the powerful electro-magnet of the induction coil. Finally, the absorption tube was therefore mounted at a distance of 30 ft. from the spectrometer and the galvanometer, and a beam of sunlight, directed into the dark room by means of a heliostat set in motion by clock-work, was brought to a focus at the centre of this tube by a long focal length lens. After emergence from the tube, the beam was made to pass through a number of diaphragms on its way to the slit of the spectrometer. With the induction coil at this distance, the galvanometer was not affected even to the slightest extent when the coil was excited. The vapour being maintained at a temperature of about 350°C . before the discharge was passed through the vapour, galvanometer

deflections were noted between 1μ , and 1.5μ at intervals of 0.02μ as this region contains the first members of the diffuse and sharp series of potassium, viz., 1.18μ and 12.5μ and the first two members of the Bergmann series, 1.52μ and 1.1μ . The vapour was then raised to feeble luminiscence by passing the discharge from a small induction coil, and galvanometer deflections were noted in the same region. On account of the low value of the ionization potential of this element, even this feeble excitation was sufficient to make the vapour emit the lines $.58\mu$ and $.53\mu$, belonging to the diffuse and the sharp series. Probably on that account no appreciable absorption was exercised at 1.25μ and 1.17μ . But at 1.5μ , the first member of the Bergmann series, there was a feeble but yet distinct absorption, the galvanometer deflections before and after the discharge was passed being 12.4 and 11.3 cm. These facts confirm in a striking manner the assumption that the energy necessary for excitation of the spectral lines increases in the order : principal ; diffuse ; sharp ; Bergmann, etc.

The results of this experiment together with those of absorption of the non-luminous vapour may be taken to be not only a striking confirmation of the view put forward in these pages regarding the origin of spectral lines, but also a clear proof of the fallacy of Seeliger's views. The electrical method is always misleading as will be seen from the conflicting views advanced from time to time by Stark.

Refraction and Dispersion of Potassium Vapour.—Among the various optical properties of a vapour, the phenomenon of refraction and dispersion presents several problems of vital importance. For an accurate knowledge of the absolute values of ' μ ' of the vapour and its dispersion throws a flood of light on the atomic constitution of matter, towards a satisfactory solution of which so much attention is directed now-a-days.

Prof. R. W. Wood, in the course of his investigations on the optical properties of sodium vapour, made an exhaustive study of refraction and dispersion of the vapour of the element by means of a Jamin's interferometer (*Phil. Mag.*, September 1904), and found that the behaviour of the vapour could be completely represented by Sellmeier formula. Later, Messrs. Cuthbertson and Pan Metcalfe (*Phil. Trans. A.*, Vol. 207, p. 135, 1908), in the course of their investigations on the refractive indices of vapours of different substances, tried to find the refraction and dispersion of potassium vapour as it seemed likely to yield results of similar interest. But they subsequently found that the chemical difficulties were so great that in spite of numerous attempts they found it impossible to determine the absolute values with the apparatus they employed, as potassium vapour attacked both glass and silica, and consequently they gave up the metals of the alkali group. As far as the author is aware, no attempt has been made since then to find the absolute values of the refractive index of the vapour for different wave-lengths. Besides this, the analysis of dispersion enables us to

estimate the number of electrons resonating to light vibrations. For, according to the electron theory of dispersion, we have—

$$n^2 (1 - \kappa^2) = 1 + \sum \frac{4 \pi N e^2}{m} \cdot \frac{(\nu_o^2 - \nu^2)}{(\nu_o^2 - \nu^2)^2 + \nu^2 \nu'^2}$$

$$2n^2 \kappa = \sum \frac{4 \pi N e^2}{m} \cdot \frac{\nu \nu'}{(\nu_o^2 - \nu^2)^2 + \nu^2 \nu'^2}$$

where ν_o is frequency of the absorbable wave-length ;

N is the number of absorption centres ,

ν is any other frequency at which the dispersion is measured ;

ν' is the damping factor ;

e and m are charge and mass of electron

According to this theory, absorption is therefore characterized by ν the oscillation frequency, ν' the damping factor, and N the number of electrons per c. cm

The principal series of all alkali metals consists of doublets, the separations of which increase with the atomic weight, and we have seen that when a beam of continuous light is passed through the vapour of these metals the resulting spectrum shows absorption of the lines of the principal series. From the results of anomalous dispersion or from the measurement of the absorption co-efficient at the place of maximum absorption we can say what fraction of the total number of atoms absorb light of each particular wave-length of the doublets of this series. The experimental results we chiefly owe to Bevan,* Rogestwensky,† Futchtbauer,‡ and Ladenburg§. The measurements of Bevan were rough, and must now be discarded in favour of those of Futchtbauer and Ladenburg. The result is so striking that without going into details of these experiments it may be stated that for corresponding doublets of all the principal series of the alkali metals, the intensities of the long-wave and of the short-wave lines have a definite ratio, and this ratio for the pairs (1,s - m,p) is equal to 1 . m. Bevan for the first time raised also the question of the influence of temperature on the constants of the dispersion formula, in a paper on "Dispersion in Vapours of the Alkali Metals." (*Proc. Roy. Soc.*, Vol. 85, pp. 54—58, 58—76, 1911) where he pointed that an increase might be expected in the ratio. Rogestwensky, in a paper on "The Simple Relations in the Spectra of the Alkali Metals" referred to above, pointed that the ratio seems to be independent of temperature ; while Miss Marian Baxter recently in a paper on "The Dispersion of Light by Potassium Vapour" (*Phil. Mag.*,

* Bevan · *Proc. Roy. Soc.*, London, 83, pp. 421—428 , 84, pp. 209—225 ; 85, pp. 54—58 , 58—76.

† Rogestwensky *Trans of Optical Institute, Petrograd*, Vol. II, No. 13, and 14, 1921.

‡ Futchtbauer · *Phys. Zs.*, Vol. 21, pp. 322—24, June 15, 1920, *Zs. F. Physik*, Vol. 4, 3, pp 337, of 1921, and *Science Abstracts*, 1922, A, 1921.

§ Ladenburg ; *Zs. f. Physik*, Vol, 4, 4, p 469 of 1921.

290—300, September 1921) by using Jamin's interferometer showed that a_1/a_2 diminished with increase of temperature. The aim of this investigation is therefore to find the absolute value of refractive index of the vapour for different wave-lengths at different temperatures, and to find the influence of temperature on the absorption centres of the red and violet doublets of potassium.

Experimental Arrangement.—In these experiments, the experimental tube consists of a thin seamless steel tubing about 16 cms. long and $1\frac{1}{4}$ cms. in diameter. The tube was furnished with two small water boxes against the ends and two small lateral tubes were brazed into the steel wall, one at each end for connexion with the pump and gas-generator. The ends of this tube and another tube of exactly the same length (to be used as the compensating tube) were closed with plane parallel plates of glass cemented to the tube with the best sealing wax. All these four pieces were cut from the same plate of glass supplied by Adam Hilger & Co. The space between the two water boxes on the experimental tube was covered with a layer of asbestos over which was wound the heating coil of Eureka. On this heating coil was wrapped two or three layers of asbestos to prevent loss of heat.

A pretty large quantity of fresh metal was cut into strips and introduced into the middle of the tube. Then by connecting the tube to a gas-generator, pure dry hydrogen was passed through the tube for some time and thus the potassium was kept in an atmosphere of hydrogen.

One of the difficulties generally experienced in work with metals of the alkali group is the rapid distillation of the metal to the colder parts and the consequent deposition on the glass plates which would seriously hamper the progress of the experiment. After many trials this difficulty was got over in these experiments by a simple device. Near the water boxes two turns of fine resistance wire were wound and a sufficiently large current of electricity was passed through these, throughout the experiment, with the result that the vapour of the metal was entrapped within the space between the water boxes, even when the tube was raised to a high temperature by passing a current through the heating coil, and it was found that the conditions were quite steady and observations could be made for any length of time.

In these experiments the determinations were made by means of a Rayleigh interferential refractometer, the distance between the two interfering streams being 20 mm. nearly. A beam of sunlight directed into the dark room through a hole in the shutter by means of a heliostat set in motion by a clock-work was concentrated on the slit of the interferometer by means of a convex lens. And the experimental tube and the compensating tube were mounted on a suitable frame on a stand provided with levelling screws and their position adjusted, such that the two tubes were in the path of the two interfering streams of light. The slits of the interferometer were kept horizontal, and the horizontal system of interference fringes obtained by the interferometer was

received on the vertical slit of a Hilger wave-length spectrometer, the telescope of which was furnished with a shutter eye-piece.

This eye-piece has two shutters which can be moved from either side, in the focal plane so as to cover any desired part of the field, thereby obscuring the remaining portion of the spectral region. It was also provided with a metal pointer the extremity of which was ground exceedingly fine and polished bright and could be illuminated from above by a small mirror. And this pointer could be adjusted by screws, such that it was always in coincidence with a particular fringe in the beginning. When the metal (potassium) in the experimental tube was vaporized, the number of bands which passed the tip of the pointer in the field of view of the telescope could be conveniently counted during evaporation and condensation.

We know that $n\lambda = (\mu - 1) l$

where n is the number of bands observed to pass the fiducial mark :

λ is the wave-length of the radiation ; and

l the length of the vapour column.

The experimental tube having been filled with dry hydrogen gas was subjected to a preliminary heating to about 350° C. by passing a suitable current through the heating coil. While hot the tube was exhausted by a Geryk vacuum pump down to 1 mm. so that the vapour of oil and the occluded hydrogen were removed and the tube contained only dry potassium in vacuum. The compensating tube also was exhausted down to a few mm. Then by passing the requisite current through the heating coils the tube was raised to the desired temperature and the number of bands that passed the fiducial mark in the field of view of the telescope both during evaporation and condensation was observed, and the same thing was done a number of times and the mean value was taken. The results of measurements at the different temperatures are given in the following Table (No. VII). In calculating the values the practice of reducing the refractivities to 0° C. and 760 mm. was not adopted as we have no information regarding the density of vapour at different temperatures, nor is it convenient for use in many investigations in the case of those gases and vapours which do not conform to the laws of Boyle and Gay Lussac closely.

It is evident from these results that the potassium vapour behaves just like sodium vapour in that all waves on the blue side of the first members of the principal series travel in the vapour with a higher velocity than in vacuum.

In this connexion it is also interesting to note that when the temperature of the tube was raised very high the fringes were very much attenuated, even to the extent of complete blurring, and this attenuation was probably due to a violent molecular agitation and impact similar to that published by O. Guoy (*J. de Physique et la Radium*, pp. 3—11, July 1920).

A knowledge of the absolute values of μ of the vapour for different wave-lengths and at different temperatures enables us to find the influence of temperature on the constants of the dispersion formula (Sellmeier).

TABLE NO. VII.

Temperature	6050	5893	5837	5750	5460	5270	5184
Number of fringes passing across the fiducial mark at wave lengths							
t'	135	12	11	9.4	7.6	5.5	4
t''	...	24.5	22	18.5	14	9.5	7
t'''	34	29	23.5	18.5	15
Refractive index for wave lengths							
t'	9999395	99994762	99995245	99995996	99996926	99997853	99998464
t''	.	9998931	99990487	99992119	99994338	99996291	99997313
t'''	9998530	9998765	99990494	9999277	99994241

$$\text{For, we know } \mu^2 - 1 = \frac{a_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{a_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

where λ_1^2 and λ_2^2 are the wave-lengths of the two absorption lines.

$$a_1 = (N_1 e^2 \lambda_1^2) / (m \Pi c^2)$$

$$a_2 = (N_2 e^2 \lambda_2^2) / (m \Pi c^2)$$

N_1 and N_2 are the number of electrons in 1 c. cm. corresponding to the two absorption lines ;

e and m are charge and mass of the electron ; and
 c is the velocity of light.

$$\therefore \frac{1}{a_2} = \frac{N_1 \lambda_1^2}{N_2 \lambda_2^2} \text{ and } \frac{N_1}{N_2} = \frac{a_1}{a_2} \left(\frac{\lambda_2}{\lambda_1} \right)^2$$

Thus by finding the ratio of the constants a_1 and a_2 we can find N_1/N_2 .

Though the experiments in this direction are not yet complete, from the refractive index values determined at the three different temperatures used in the above experiment, a_1/a_2 values are calculated, and they are

t'	448	480
t''	430	440
t'''	550	590

These results tend to show roughly that the ratio is independent of the vapour density ; at any rate it does not diminish with increase of temperature.

SUMMARY OF RESULTS AND CONCLUSIONS

The results which have been accomplished in this work may be briefly summarized as follows —

1. The number of members of the principal series ($1,s - m,p$) has been raised from 24 to 30.*

2. The channelled spectrum accompanying the first members of this series has been photographed and fifteen bands have been recorded.

3. It has been shown that the first eight members of the principal series are accompanied by satellites which are not found in the emission spectrum, and some of which have not been recorded by the previous investigators.

4. The combination pair ($1,s - 3,d$) has been reversed, which not only confirms the presence of a satellite in the diffuse series but also suggests that the lines of the fundamental series should consist of doublets with a constant separation. Further, it is a direct negation of the selection principle in its present form.

5. The line 4120 A.U. recently observed by Datta in Lord Rayleigh's vacuum arc lamp as an abnormally faint line has been reversed.

6. The absorption spectrum at high temperatures showed among other lines which seem to correspond to the lines of the associated series, line 4831 which is undoubtedly the same as the emission line observed by Robertson in his experiments on electrodeless discharge through potassium vapour (*Phys. Rev.*, May 1922). It has been found that this is the combination line $1,p - 8,p$, which is very significant in view of the fact that one of its terms is ($1, p$) as it appears only at high temperatures along with $1,p - m,d$ lines.

7. The infra-red emission spectrum of potassium has been studied and 11 lines have been recorded between 0.96μ and 3.7μ . The existence of the line 3.67μ and 2.72μ , which were found by Moll and Paschen respectively, but not found by later investigators has been confirmed, and a new line was found at 1.2μ .

8. The absorption spectrum of the vapour in the infra-red has been studied and it has been found that the non-luminous vapour does not exercise any selective absorption.

9. By distilling the vapour into a discharge tube under a high vacuum, and by passing a feeble discharge, it has been found that the vapour exercises feeble but distinct absorption at 1.51μ .

10. The importance of the study of absorption in the infra-red by the non-luminous and luminous vapours on the problem of temperature radiation and the origin of the spectral lines has been shown.

11. By a Rayleigh Interferential Refractometer, refraction and dispersion of the vapour in the visible region were studied, and the absolute

* Simultaneously with the author, Datta, working with a 10 ft concave grating raised the series to 42

values of μ have been found for different wave-lengths, which, as far as the author is aware, have not been determined by the previous investigators, and a cursory examination was made of the influence of temperature on the ratio of the number of vibrating electrons corresponding to the red and the violet doublets

EXPLANATION PLATES.

I. Apparatus as it stood in my study of the absorption in the ultra-violet.

I-A. Photograph showing the gradual development of the principal series with increase of vapour density.

II. Channelled spectrum accompanying 1,s — 2,p.

III. Satellites accompanying 1,s — 4,p ; the one at higher temperature distinctly shows four satellites, and a careful examination of the main line shows that it is split into two.

IV. Photograph showing 4119'1 and the first seven members of the series.

IV-A. Enlarged photograph of the principal series which shows clearly that the ninth member also has a faint satellite on the right.

V. Photograph showing gradual development of 5780 and the narrow transparent region between this and the violet band at about 1000° C. (Blue violet channelled space which has become a dark band at this temperature.)

V-A. Absorption of 1,s — 3,d.

VI. Photograph showing the discharge tube used for examining the structure of 1,s — 3,d and for studying absorption of electrically luminiscent vapour.

VII. Brass fittings showing the cylindrical electrodes of Pt.

VIII. Arrangement adopted for studying the structure of 1,s — 3,d.

X. Diffraction pattern of the above line with a Lummer plate.

XI. Modified form of arc used in the study of emission spectrum in the infra-red.

XII. Plan of infra-red spectrometer, Paschen galvanometer, and standardizing potentiometer.

XIV & XV. Incident and transmitted energy curves in infra-red absorption.



APPENDIX.

LIST OF PAPERS CONTRIBUTED TO THE VARIOUS SCIENTIFIC JOURNALS.

1. SOUNDS OF SPLASHES.

Phil. Mag. and Journal of Science London, Nov. 1921.

2. COUPLED VIBRATION BY MEANS OF DOUBLE PENDULUM.

Phil. Mag., March 1922.

3. THREE MAGNETICALLY COUPLED OSCILLATING CIRCUITS.

Phil. Mag., March 1922.

4. SURFACE TENSION OF SOAP SOLUTIONS AT DIFFERENT CONCENTRATIONS AND THE SHAPE OF THE PARTICLES IN THESE SOLUTIONS (In 2 parts).

Part 1 read before the Madras Session of the I.S.C. and published in *Phil. Mag.*, April 1922, and reported in *Kolloid Zeitschrift*.

Part 2 read before the Lucknow Session of the I.S.C. and submitted to *Phil. Mag.*

5. ANDERSON BRIDGE AND MEASUREMENT OF SMALL INDUCTANCES.

Read before the Lucknow Session of I.S.C.

6. A MODIFIED FORM OF DOUBLE SLIT SPECTROPHOTOMETER.

Read before the 9th Annual Meeting of the I.S.C., and published in *Phil. Mag.*, April 1922, and reported in *Journal de Physique*.

7. EMISSION AND ABSORPTION OF THE HALOGENS IN THE VISIBLE AND ULTRA-VIOLET REGIONS, AND THE EFFECT OF TEMPERATURE ON ABSORPTION.

Read before I.S.C., held in Madras, and Annual Science Convention of the Indian Association for the Cultivation of Science, 1923. (*Phil. Mag.*, May 1923.)

INVESTIGATIONS ON THE OPTICAL PROPERTIES OF POTASSIUM VAPOUR.

8. ABSORPTION IN THE ASSOCIATED SERIES.

Nature 19, August 1922.

9. ABSORPTION AT HIGH TEMPERATURES AND ITS BEARING ON THE SELECTION PRINCIPLE OF THE QUANTUM THEORY.

Astro-physical Journal, April 1923.

C51:7: (E112)

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10. ABSORPTION IN THE VISIBLE AND THE ULTRA-VIOLET REGIONS WITH REFERENCE TO THE PRINCIPAL SERIES (1,s — m,p.).

Phil. Mag., May 1923.

11. ABSORPTION AT HIGH TEMPERATURES.

(*Phys. Rev.*).

12. EMISSION AND ABSORPTION IN THE INFRA-RED REGION, WITH SPECIAL REFERENCE TO THE BERGMANN SERIES.

(*Pro. Ind. Association for the Cultivation of Science.*)

13. REFRACTION AND DISPERSION IN THE VISIBLE REGION. (BY AN INTERFERENTIAL REFRACTOMETER.)

A preliminary statement of the results contained in papers 8 to 13 was made before the Lucknow Session of the I.S.C

14. ABSORPTION OF ELECTRICALLY LUMINESCENT VAPOUR.

(*Pro. Ind. Association for the Cultivation of Science.*)

15. EMISSION AND ABSORPTION OF MERCURY VAPOUR IN WOOD'S LONG DISCHARGE VACUUM TUBES.

(Recently started by myself and Mr. Gunnayya.)

16. SPECTRA OF ISOTOPES.

Nature, November 3, 1923.

17. SCATTERING OF LIGHT BY CARBON DIOXIDE, NITROUS OXIDE, AND SOME ORGANIC VAPOURS.

(Read before the Physical Society, London, Nov. 9, 1923, by Lord Rayleigh, in the absence of the author.)

